Adsorption of Low Charge Density Polyelectrolyte Containing Poly(ethylene oxide) Side Chains on Silica: Effects of Ionic Strength and pH

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ABSTRACT: Adsorption characteristics of a random copolymer of poly(ethylene oxide) monomethyl ether methacrylate and methacryloxyethyl trimethylammonium chloride (PEOMEMA:METAC) on silica were studied using stagnation point adsorption reflectometry (SPAR), quartz crystal microbalance with dissipation (QCM-D), and contact angle techniques. The PEOMEMA:METAC copolymer used in this study is a low charge density polyelectrolyte, with 2% of the monomer units carrying permanent positive charges and 98% containing poly(ethylene oxide) side chains that are approximately 45 repeating units long. The surface excess was determined as a function of pH and concentration of indifferent electrolyte. It was found that the presence of a small amount of 1:1 electrolyte decreases the adsorbed amount significantly. Further, increasing the pH at a constant ionic strength, 10 mM, results in decreasing surface excess. It is suggested that the adsorption is realized via a combination of non-Coulomb interactions between the poly(ethylene oxide), PEO, grafts and protonated silanol groups at the silica−solution interface and an electrostatic interaction between the charged segments and the oppositely charged surface. Increasing pH and/or salt concentration results in progressive charging of the silica surface with the consequent decrease in affinity between silica and PEO, explaining the decrease in the adsorbed amount of the polymer.

Introduction

Interfacial properties of polyelectrolytes have gathered considerable research interest in recent years. Adsorption of polyelectrolytes to oppositely charged surfaces gives rise to a variety of interfacial phenomena utilized for controlling colloidal stability,[1,2] building multilayer structures,[3,4] complexation,[5] etc. When discussing polyelectrolytes at oppositely charged surfaces, the main driving force for adsorption is considered to be the electrostatic interaction between surface and polymer charges. In such a case, the adsorbed amount and the resulting adsorbed layer structures are determined by the strength of the electrostatic polymer−surface attraction as well as the intramolecular and intermolecular polymer repulsion. The interfacial behavior of polyelectrolytes is in most cases predominantly determined by the polyelectrolyte charge density, the surface charge density, and the amount of screening electrolyte,[6−8] which are the main factors governing the electrostatic interactions in the system. It has been established both theoretically and experimentally that reducing the charge density of a polyelectrolyte and/or the surface charge leads to thicker adsorbed layers with larger fractions of loops and tails extending into solution.[8−10] The effect of simple electrolyte concentration on polyelectrolyte adsorption is somewhat more complicated. Assuming electrostatically driven adsorption, adding salt leads to a decrease of adsorbed amount due to screening of the electrostatic surface−segment attraction.[7] Furthermore, small surface counterions will compete more successfully with the polyelectrolyte for neutralizing the surface charge at higher ionic strength.[11] The onset of this screening reduced adsorption regime depends on the surface and polyelectrolyte charge densities. For polymers of low to moderate charge adsorbing on moderately charged surfaces the screening reduced regime is usually observed in solutions containing 0.1−1 M 1:1 electrolyte.[6,12] In many cases, however, there are nonelectrostatic surface−polymer interactions present that contribute to the total adsorption free energy of a polyelectrolyte.[6] In this case the surface excess initially increases with ionic strength before it decreases again at even higher salt concentrations.[13] Among the secondary polymer−surface interactions hydrogen bonding deserves special attention. It has been long recognized that polymers possessing electron donor groups, such as polyethers and polyacrylamides, adsorb onto silica surfaces, and the primary adsorption mechanism has been described as hydrogen bonding.[14−17] Recently, charged polymers with variable charge densities have been assembled into multilayer structures via combination of hydrogen-bonding and electrostatic interactions.[18,19]

In this report we address the adsorption behavior of a low charge density cationic copolymer having a high side-chain density of about 45 segments long poly(ethylene oxide) chains, also known as poly(ethylene glycol). The cationic comb polyelectrolyte used in this study is thus expected to be able to adsorb onto silica surfaces with both its slightly charged backbone and its uncharged side chains. This provides an opportunity to

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study a polymer adsorption driven by both electrostatic and nonelectrostatic polymer−substrate interactions.

Materials and Methods

Materials. Poly(ethylene oxide)-2000 methyl ether methacrylate (PEOMEMA) as 50% aqueous solution from Aldrich and methacryloxyethyl trimethylammonium chloride (METAC) as 70% aqueous solution from Polysciences, Inc., were used as received. Azobis(isobutyronitrile) (AIBN) from Reachim was recrystallized from methanol and dried in a vacuum at 30 °C. 2-Propanol (Fluka) and chloroform (Fluka) were used without further purification. Sodium hydroxide monohydrate, hydrochloric acid, and sodium nitrate (Suprapur) were purchased from Merck and used as received. Water was purified with RiOS-8 and Milli-Q plus 185 units from Millipore.

Thermally oxidized silicon wafers were purchased from Wafer Net, Germany. The wafers were cut to size and conditioned by immersion in a solution mixture of $H_2O/HCl/H_2O_2$ (66:21:13) at 75−80 °C for 10 min. The plates were then removed and rinsed in Milli-Q water several times before immersion in a solution mixture of $H_2O/NH_3/H_2O_2$ (71:17:12) at 75−80 °C for another 10 min. Finally, the plates were rinsed with copious amounts of Milli-Q water and stored under absolute ethanol prior to use. The above procedure yielded fully water wetted silica substrates. The thickness of the oxide layer was determined ellipsometrically and found to be 100 ±1 nm. The same procedure was used to prepare glass slides for contact angle determination.

For QCM-D measurements silica-coated quartz crystal oscillators were purchased from q-sense, Sweden. The crystals were cleaned by ultrasonication for 20 min in 1% Hellmanex cleaning solution. The silica-coated side was then exposed to a heated $H_2O/NH_3/H_2O_2$ (71:17:12) mixture for 10 min followed by thorough rinsing with Milli-Q water. The crystals were used immediately after cleaning.

Polymer Synthesis. Free-radical copolymerization of PEOMEMA with METAC was carried out in a polymerization tube under nitrogen atmosphere at 60 °C in a 57:43 mixture of 2-propanol and water. The overall monomer concentration in the solution was 30%. The mixture was allowed to react for 20 h in the presence of 0.3% AIBN as initiator. Specifically, 0.1362 g of AIBN (0.83 mmol), 27.18 g of 50% aqueous solution of PEOMEMA (6.53 mmol), 0.040 g of 70% aqueous solution of METAC (0.133 mmol), and 18.2 g of 2-propanol were placed in a polymerization tube. The tube was purged with nitrogen gas for 15 min and inserted in an oil bath kept at 60 °C. After 20 h the reaction mixture was left to cool to room temperature, and the tube content was quantitatively transferred into the Visking dialysis tubing 27/32 (Serva, pore size 24 Å, exclusion limits 8−15 kDa) using as small amount of distilled water as possible. The copolymer solution was dialyzed against 0.002 M aqueous HCl for 5 days, changing the solvent two times per day. The dialyzed solution was concentrated to a viscous liquid using a rotating evaporator. The product was then extracted with chloroform and dried in a Petri dish at room temperature for 2−3 days. Finally, the product was dried in a vacuum oven at 60 °C for 24 h to give 12.3 g of the copolymer (yield 90.3%).

The molecular weight of the macromonomer PEOMEMA was determined by gel permeation chromatography (GPC) using a Waters 2410 RI detector and a Wyatt DAWN EOS laser light scattering detector. The columns used were ultahydrogel linear + TSK GMP2000. Aqueous solution of 0.3 M $NaNO_3$ at pH ~ 10 was used as eluent at a flow rate of 0.8 mL/min. The composition of the copolymer was calculated according to chlorine content determined by argentometric titration. The average molecular weight of the macromonomer PEOMEMA was determined to be 2080 g/mol. Thus, its semistructural formula can be represented as $CH_2C(CH_3)COO(CH_2CH_2O)_{45}CH_3$. The structural formula of METAC is $CH_2C(CH_3)COOCH_2CH_2N(CH_3)_3Cl$, and the molecular weight of this monomer is 208 g/mol. The calculated amount of Cl for a copolymer PEOMEMA:METAC = 98:2 mol % is 0.035%. This polymer will henceforth be referred to as $PEO_{45}MEMA$:METAC-2, where the subscript 45 is the average number of repeating units in the side chains and the digit 2 refers to the percentage of charged monomers in the backbone. This agrees well with the Cl amount of 0.034% determined experimentally, suggesting that the composition of the copolymer is nearly identical to that of the monomer mixture; i.e., the copolymer contains about 2 mol % of monomeric units carrying a positive charge. The copolymer has, according to static light scattering measurements, a weight-average molecular weight of 470 kDa. The polydispersity as estimated by GPC is $M_w/M_n = 2.8$. A simple estimation from the weight-average molecular weight indicates that the average macromolecule consists of approximately 230 monomeric units, four to five of which are carrying a positive charge. The structure of the copolymer $PEO_{45}MEMA$:METAC-2 is shown in Figure 1.

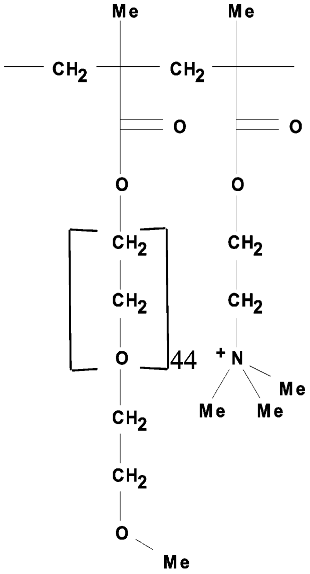

Figure 1. Structure of the repeating units of $PEO_{45}MEMA$:METAC-2 copolymer.

Methods. Stagnation point adsorption reflectometry (SPAR) experiments were performed in a temperature-controlled room at 25 ± 1 °C. An elaborate description of the technique is given elsewhere.[20,21] In brief, linearly polarized laser light is reflected from the substrate−water interface at an angle close to the Brewster angle. The reflected light is split into its parallel and perpendicular polarization components I_p and I_s, and the respective intensities are measured by means of photodiodes. The ratio I_p/I_s, defined as the signal S, is continuously recorded during an experiment. The change in the signal (ΔS) upon adsorption is related to the surface excess, Γ, via

$$\Gamma = \frac{1}{A_s}\frac{\Delta S}{S_0}$$

The parameter A_s, also known as the sensitivity factor (relative change in S per unit surface excess), is determined by treating the system as a four-layer optical model (Si−SiO_2, adsorbed layer, medium) within the framework of Fresnel reflectivity theory.[20]

Controlled transport of material to the surface was realized by means of stagnation point flow. At the stagnation point the hydrodynamic flow is zero, and the material flux, J, toward the surface is given by[20]

$$J = 0.776(\alpha U)^{1/3}(D/R)^{2/3}C$$

where U is the average fluid velocity, D is the diffusion coefficient of the adsorbate, R is the radius of the inlet tube, C is the concentration of the adsorbate, and α is a parameter which depends on the Reynolds number, radial distance to the stagnation point, h, and the cell geometry (h/R). All of the above-mentioned variables can be controlled, allowing a reproducible material transport to the surface.

The quartz crystal microbalance with dissipation (QCM-D) setup was manufactured by q-sense, Sweden. The QCM-D allows for precise determination of the mass added to a sensor crystal surface by monitoring changes in its resonance frequency.[22] AT-cut quartz crystals are sandwiched between thermally evaporated gold electrodes and excited in thickness shear mode oscillation. The resonant frequencies (fundamental and up to three harmonics) are recorded in real time and related to the mass added to the surface via[23]

$$\Delta m = -nC\Delta f$$

where Δm is the added mass, n is the harmonic order, and Δf is the shift in resonance frequency. C is a sensitivity constant dependent on the properties of the crystal. For the crystals used in this work $C = 17.7$ ng cm^{-2} Hz^{-1}. It should be stressed that the QCM-D is sensitive to the total mass added to the sensor crystal surface. This includes the adsorbate as well as solvent incorporated into the layer.

Simultaneously, the dissipation factor, D, is recorded. It is defined as the ratio between the energy dissipated and stored in the crystal during a single oscillation:

$$D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}}$$

The change in dissipation value provides information about changes in the coupling between the oscillating surface and the liquid occurring as a result of adsorption. It is generally found that thick and loosely bound layers dissipate energy more efficiently than thin and rigid ones. Thus, the change in dissipation is larger in the former case.

Contact angles were determined by the Wilhelmy plate method. Freshly cleaned glass slides were attached to a balance (Krüss K12), immersed into polymer solution, and allowed to equilibrate for 120 min. The advancing contact angle was determined via the following relation:

$$F = 2\gamma(w + t)\cos\theta - \Delta\rho gwtd$$

where F is the force exerted on the balance, γ is the surface tension of the liquid (measured separately), θ is the contact angle, $\Delta\rho$ is the density difference between the investigated solution and air, g is the gravitational acceleration, w and t are the width and thickness of the plate, and d is the immersion depth.

Results

In this section we will first present adsorption data for the polymer PEO$_{45}$MEMA:METAC-2 obtained under various solution conditions. Next, some results obtained by the QCM-D and Wilhelmy plate techniques will be reported. The data obtained will be utilized to elucidate the driving force for adsorption and to gain some information on the adsorbed layer structure.

The equilibrium surface excess on silica as a function of PEO$_{45}$MEMA:METAC-2 bulk concentration at different background electrolyte concentrations is illustrated in Figure 2. The plateau value of the surface excess is reached at a bulk polymer concentration of 5 ppm in all cases. The surface excess, however, is influenced dramatically by the presence of salt. Adding 1 mM NaNO$_3$ reduces the plateau surface excess from approximately 1.7 mg/m^2 for adsorption from salt-free solutions to 0.7 mg/m^2. In 10 mM NaNO$_3$ the adsorption is further reduced to a plateau value of 0.2 mg/m^2 and is virtually undetectable for bulk concentrations below 5 ppm. No adsorption could be detected in 100 mM NaNO$_3$.

The surface excess at pH 6 and pH 2 is compared in Figure 3. The values obtained at pH 2 are considerably lower than those obtained at pH 6. At pH 2 the silica surface is uncharged; hence, the driving force for adsorption is in this case expected to be of nonelectrostatic origin. The plateau surface excess at pH 6 and pH 2 is plotted in Figure 4 as a function of NaNO$_3$ concentration. For the measurements at pH 2, HCl was added to a total concentration of 10 mM in order to adjust the pH. As noted earlier, the plateau surface excess at pH 6 decreases rapidly with increasing ionic strength, and no adsorption could be detected for NaNO$_3$ concentrations above 10 mM. At pH 2 the surface excess shows a much weaker dependence on the amount of added salt. A reduction from 1.15 to 0.75 mg/m^2 is noted between 0.1 and 10 mM NaNO$_3$, with no further decrease in adsorption upon increasing the NaNO$_3$ concentration to 100 mM. Clearly, adding salt has little influence on adsorption to uncharged silica but a significant effect when the silica surface is negatively charged. This will be discussed further below.

The results obtained for PEO$_{45}$MEMA:METAC-2 adsorption as a function of pH are summarized in Figure 5. The broken line traces the data obtained at a constant

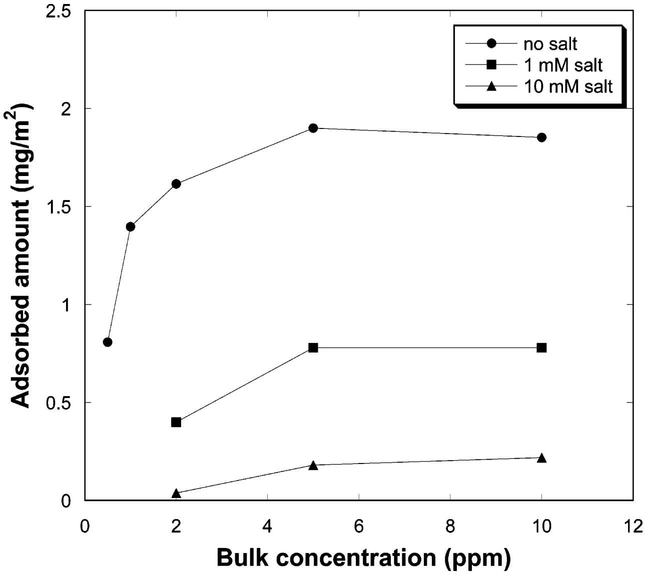

Figure 2. Adsorption isotherms of PEO$_{45}$MEMA:METAC-2 on silica at pH 6 and various ionic strengths.

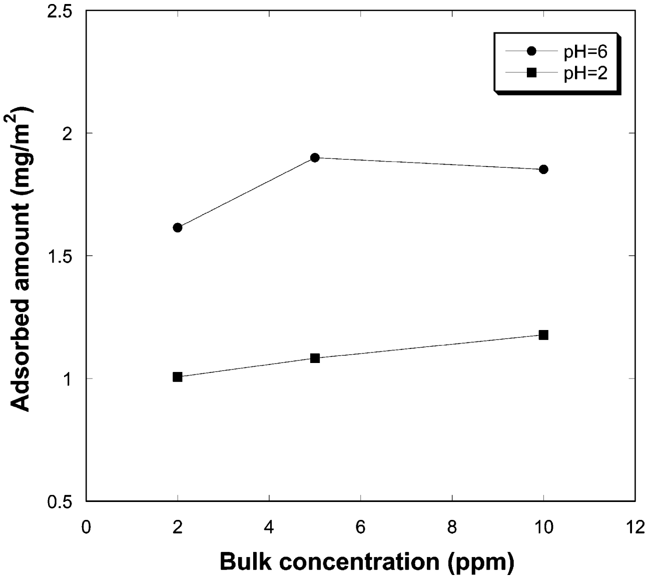

Figure 3. Adsorption isotherms of PEO$_{45}$MEMA:METAC-2 on silica at two different pH values.

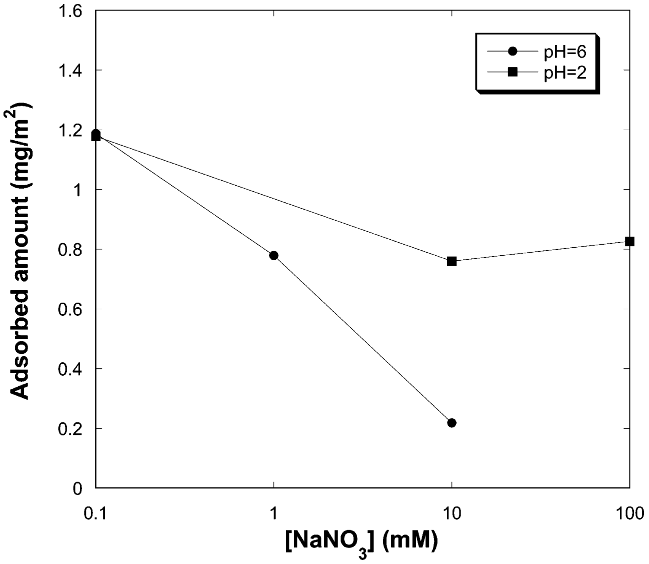

Figure 4. Effect of $NaNO_3$ concentration on the plateau adsorbed amount of PEO_{45}MEMA:METAC-2 on silica at two different pH values.

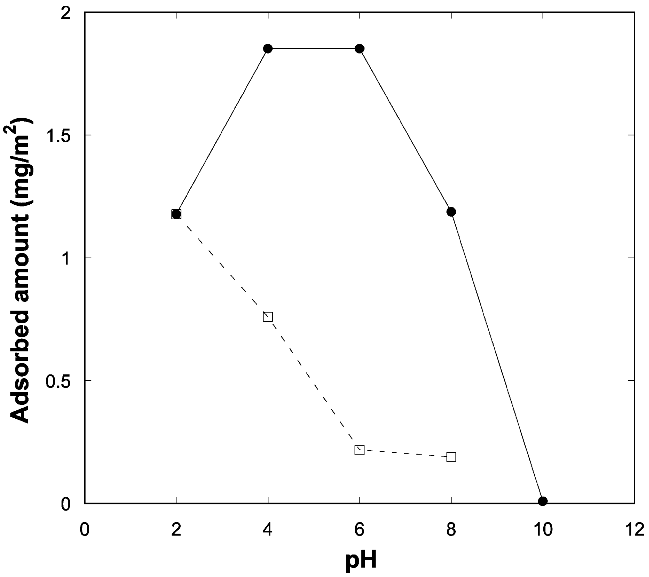

Figure 5. Plateau adsorbed amount of PEO_{45}MEMA:METAC-2 vs pH of the solution. Filled symbols represent data where the ionic strength has not been controlled but is given by the added acid or base. Unfilled symbols represent data where the ionic strength has been kept constant at 10 mM.

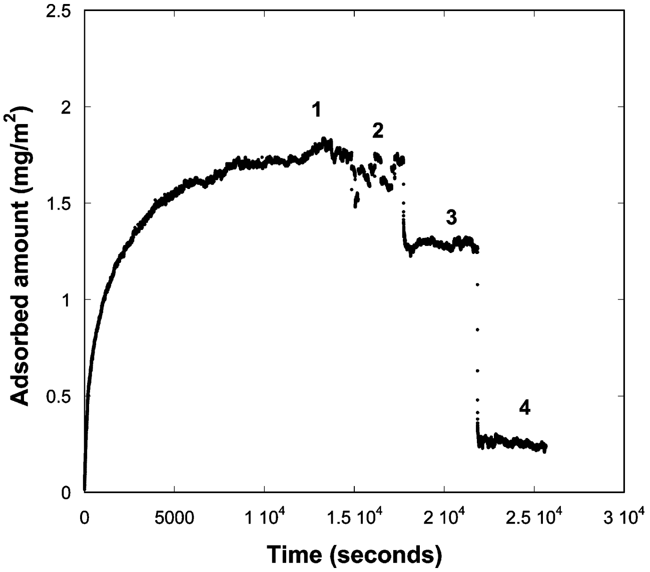

Figure 6. Desorption of PEO_{45}MEMA:METAC-2 upon changing solution conditions: 1, adsorption from 10 ppm salt-free polymer solution at pH = 6; 2, rinsing with Milli-Q water; 3, rinsing with 0.1 mM $NaNO_3$; 4, rinsing with 0.1 mM NaOH (pH = 10).

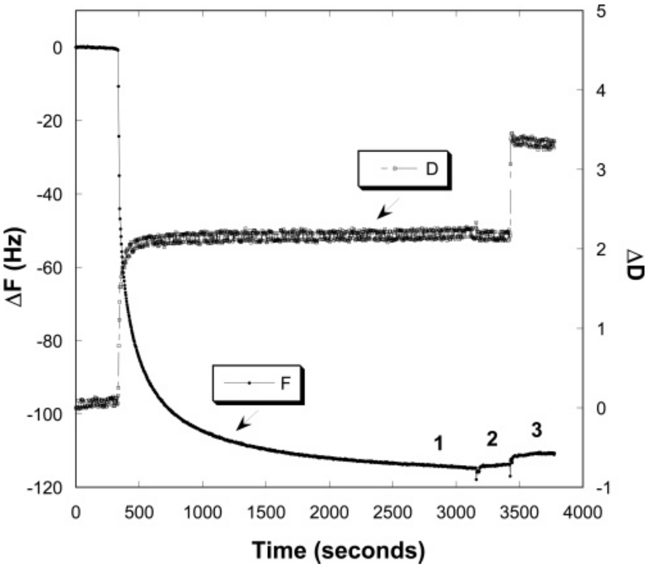

Figure 7. Plots of data from QCM-D showing frequency and dissipation changes vs time: 1, PEO_{45}MEMA:METAC-2 adsorption from 10 ppm solution also containing 10 mM HCl (pH = 2); 2, rinsing with polymer-free 10 mM HCl solution; 3, rinsing with polymer-free 10 mM $NaNO_3$ solution (pH = 6).

ionic strength of 10 mM. In this case the surface excess decreases monotonically with increasing pH. The solid line connects data points for the case when the solutions were not "buffered" in terms of total electrolyte content, but only the appropriate amounts of HCl or NaOH were added to achieve the desired pH. In this case the surface excess initially increases as the pH is increased from pH 2 and reaches a maximum in the pH range 4−6. At alkaline pH the adsorbed amount rapidly decreases, and at pH 10 the adsorption is virtually inhibited. To further illustrate the effect of varying pH at constant ionic strength, the experiment depicted in Figure 6 was performed. The polymer was initially adsorbed from salt-free solution at pH 6 (region 1). This was followed by rinsing with pure Milli-Q water (region 2), 0.1 mM $NaNO_3$ (region 3), and finally 0.1 mM NaOH (region 4). During the last two steps the total ionic strength is kept constant at 0.1 mM; however, the pH increases from 6 to 10. Clearly, this has a dramatic effect on the surface excess. While little desorption occurs upon rinsing with pure water, rinsing with 0.1 mM $NaNO_3$ results in approximately 25% of the adsorbed polymer being desorbed. Replacing this solution with 0.1 mM NaOH leads to a further strong decrease of the surface excess to approximately 0.24 mg/m^2, corresponding to approximately 85% polymer removal from the surface. Since the ionic strength is kept constant, the difference between regions 3 and 4 is solely due to the change in surface charge density caused by the pH increase. Using the data of Bolt[24] for the surface charge density of fully hydroxylated silica sols, it can be shown that the surface charge density increases from 3.2 mC/m^2 in 0.1 mM 1:1 electrolyte at pH 6 to 67.3 mC/m^2 at pH 10.

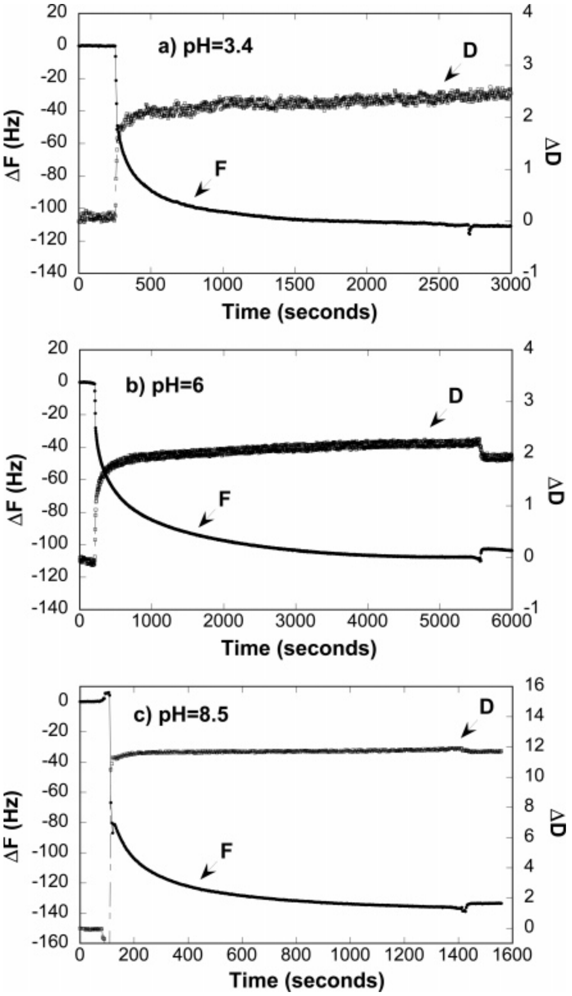

Figure 8. Plots of data from QCM-D showing frequency and dissipation changes vs time for PEO$_{45}$MEMA:METAC-2 adsorption from 10 ppm solution at various pH. The step in the curves at the end of each experiment corresponds to rinsing with polymer-free solution of the same pH as used during the adsorption step.

Adsorption of PEO$_{45}$MEMA:METAC-2 at the silica water interface as monitored with the QCM-D technique is illustrated in Figure 7. Both frequency and dissipation change traces are shown. In region 1 the polymer is adsorbed at pH 2. Adsorption results in a decrease in resonance frequency and an increase in dissipation. In region 2 the chamber is flushed with a polymer-free HCl solution at pH 2. A minor increase in resonance frequency and decrease in dissipation indicate that some small amount of polymer desorbs during this step. In region 3 the 10 mM HCl solution is replaced with a 10 mM NaNO$_3$ solution. The resonance frequency increases slightly; however, a more marked difference is observed in the dissipation factor that increases by about 30%. This indicates that the adsorbed layer swells considerably upon exposure to the NaNO$_3$ solution. It should be remembered that QCM-D is sensitive to the total mass oscillating with the sensor surface, including any solvent associated with the adsorbate. Thus, from the data in Figure 7 it is impossible to determine the amount of polymer desorbed in region 3. As the polymer layer swells, more water is incorporated into the film, the mass of which offsets to some extent the mass loss due to polymer desorption.

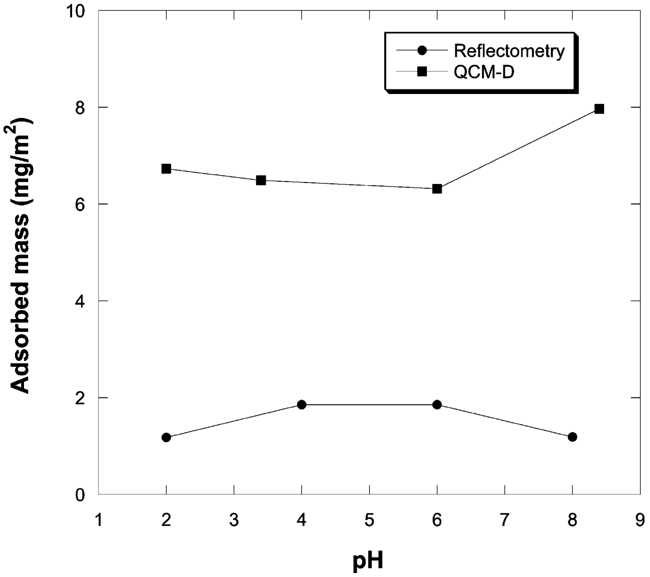

Figure 9. Comparison between plateau adsorbed amount as determined by reflectometry and the sensed mass registered by QCM-D for PEO$_{45}$MEMA:METAC-2 adsorption on silica as a function of the pH of the adsorption solution. The PEO$_{45}$-MEMA:METAC-2 concentration was 10 ppm.

The QCM-D data for PEO$_{45}$MEMA:METAC-2 adsorption from solutions at pH 3.4, pH 6, and pH 8.5 are shown in Figure 8. Similar values for the change in resonance frequency and dissipation factor were obtained for adsorption at pH 3.4 and pH 6. Adsorption from alkaline solution, however, resulted in significantly higher values for the dissipation (note the different dissipation scale in Figure 8c). This indicates that the polymers adopt significantly more extended conformations at the silica−solution interface at the higher pH value, which, in turn, results in a more efficient coupling of the crystal's shear motion to the bulk solution. The sensed mass at pH 8.3 is approximately 40% higher than at the lower pH values. As noted earlier, it is impossible to determine the surface excess of the polymer from these data since the amount of incorporated solvent is unknown. This can, however, be determined by combining QCM-D and reflectometry data. The results are presented in Figure 9. The sensed mass obtained from the change in resonant frequency was calculated using the Sauerbrey equation.[23] The sensed mass is significantly higher than the surface excess measured by reflectometry. The surface excess and the sensed mass depend on the pH in a strikingly different way. While the surface excess determined by SPAR has a maximum in the pH region between 4 and 6, the sensed mass measured by QCM-D decreases slightly in the pH range 2−6 and then increases at alkaline pH. Since reflectometry senses only the adsorbed polymer, the difference between the two curves is attributed to solvent associated with the adsorbed layer. Clearly, PEO$_{45}$MEMA:METAC-2 produces water-rich adsorbed layers. For instance, at pH 6 it can be calculated that approximately 70% of the mass sensed by the QCM-D is actually water. At pH $>$ 6 this amount increases further due to increased swelling of the adsorbed layer. Despite the fact that less polymer adsorbs at pH $>$ 6, as determined by reflectometry, its extended conformation allows for considerably more water to be incorporated into the adsorbed layer, and the net effect is an increase in the mass sensed by the QCM-D. Here it should be noted that the hydrodynamic thickness, determined by the longest tails, is not expected to change due to the decreased surface affinity at higher

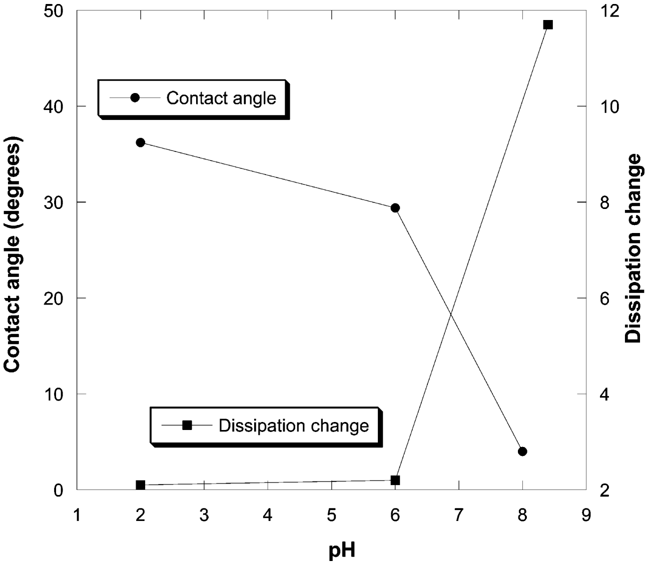

Figure 10. Contact angle and dissipation change (from QCM-D) as a function of pH.

pH.[25] The increased water content of the layer nevertheless increases the coupling to the bulk solution as monitored by the increasing dissipation factor.

Conformational changes due to variations in pH were also probed by contact angle measurements on glass slides using PEO_{45}MEMA:METAC-2 solutions. The contact angle vs pH is plotted in Figure 10 together with dissipation change data from QCM-D measurements. Adsorption of PEO_{45}MEMA:METAC-2 at low to neutral pH increases the glass contact angle substantially to values of 37° and 30° at pH 2 and pH 6, respectively. At higher pH the contact angle drops to below 10°, which corresponds to what is usually measured on freshly cleaned bare glass slides. The decrease in contact angle correlates with an increase in the dissipation factor. Clearly, at pH < 6 PEO_{45}MEMA:METAC-2 adsorbs in layers with a larger fraction of EO units bound to the surface, thus partly exposing its hydrophobic metacrylate backbone to the solution. In contrast, adsorption from alkaline solutions results in more swollen, water-rich layers. This structural difference is the reason for the more hydrophilic layer produced at the higher pH value.

Discussion

At least two aspects of the results presented in this report are unusual. First, it is observed by increasing the solution pH that the adsorption of the cationic polyelectrolyte decreases as the charge density of the negatively charged silica surface increases. Second, the surface excess in the neutral pH range is extremely sensitive to the ionic strength of the solution. To rationalize these findings, we have to recapitulate some key features of cationic polyelectrolyte adsorption on oppositely charged surfaces as well as recall the nature of the silica surface and some aspects of the adsorption of poly(ethylene oxide) onto silica.

Effect of Ionic Strength on Polyelectrolyte Adsorption. Let us consider polyelectrolytes adsorbing on an oppositely charged surface with the adsorption driven only by electrostatic interactions. In this case the surface excess decreases with increasing ionic strength.[13] This is qualitatively similar to what is observed in the present case. However, by comparing with other experimental results[12,26,27] and theoretical predictions,[13] it becomes clear that the sensitivity to the electrolyte concentration is unusually high for PEO_{45}MEMA:METAC-2 adsorption onto silica. In fact, at pH 6 even adding as little as 1 mM $NaNO_3$ reduces the surface excess to 40% of that obtained in pure water. Previously, low charge density polyelectrolytes with monomer charge densities in the range 1−10% have been investigated.[11,12,28] Typically these polyelectrolytes are acrylamide copolymers, and they exhibit a strong reduction in the surface excess at salt concentrations approximately 1−2 orders of magnitude higher than in our case.[12] These latter results are consistent with the notion that the primary driving force for adsorption is electrostatic and that salt screens the polymer−surface attraction.

If we allow for a nonelectrostatic affinity between the polymer and the surface, experimental[6] and theoretical[11,13] results show that the adsorption actually increases when a small amount of salt is added. Thus, considering the strong reduction in surface excess for PEO_{45}MEMA:METAC-2 with increasing ionic strength, it appears to be a better option to explain the results using only electrostatics than to invoke a nonelectrostatic affinity. However, we will argue that in fact the opposite is correct.

Effect of Surface Charge Density on Polyelectrolyte Adsorption. For the case of polyelectrolytes adsorbing on an oppositely charged surface from a low ionic strength solution, with the adsorption driven only by electrostatic interactions, both experimental results[29,30] and theoretical calculations[8,13] consistently demonstrate that at the plateau value of the adsorption isotherm the polyelectrolyte charges in the adsorbed layer very closely balance the charges present on the surface. Thus, as the charge density of the surface is increased, the surface excess of the polyelectrolyte increases. When the more complex situation that allows also for a nonelectrostatic affinity between the surface and the polyelectrolyte is considered, the prediction is that the surface excess increases somewhat to allow some overcompensation of the surface charge present on the substrate.[6] Also in this case the surface excess of the polyelectrolyte increases with increasing surface charge density.

The set of results presented here does not follow these trends. First of all, PEO_{45}MEMA:METAC-2 adsorbs to silica at pH = 2 where the surface is uncharged. The surface excess decreases sharply as the pH is increased (i.e., the magnitude of the surface charge density is increased), and the adsorption is completely inhibited at pH 10 despite that silica has a considerable negative surface charge capable of electrostatic interaction with the cationic groups of the polymer. It seems clear that the main surface−polymer interaction responsible for the adsorption is not electrostatic. Thus, in this respect PEO_{45}MEMA:METAC-2 does not behave as a typical polyelectrolyte, and we cannot explain the results by adding a nonelectrostatic polymer−surface affinity that is independent of pH and the ionic strength of the solution. We have to conclude that the nonelectrostatic surface affinity is important for the adsorption process and that it decreases as the pH and/or the ionic strength of the solution increases. It seems reasonable to assume that it is the PEO side chains that are responsible for the nonelectrostatic polymer−surface affinity. Hence, to rationalize our results, we have to consider the nature of the silica surface and what is known about poly(ethylene oxide) adsorption to silica.

Nature of the Silica Surface. The silica surface exposes a high density of silanol (−Si−OH) groups toward the aqueous phase. These groups can be ionized to form negatively charged $-SiO^-$ groups, and at low pH also positively charged $-SiOH_2^+$ groups can be formed. The isoelectric point of silica is about 2. Hence, at higher pH values silica is negatively charged. Fully hydroxylated silica has 4−5 Si−OH groups per nm^2 as determined by pH titration of silica sols.[31] As pointed out by Ong et al.[32]and later confirmed by Ying et al.,[33] there are two distinctly different silanol group populations at the silica surface, isolated silanols not bound by hydrogen bonds to other silanol groups with $pK_a = 4.9$, and hydrogen-bonded silanols which start to dissociate at significantly higher pH ($pK_a = 8.5$). The amount of the isolated silanols has been estimated to be approximately 20% of the total silanol group amount.[33]

Effect of pH on Adsorption of Poly(ethylene oxide) Containing Polymers to Silica. The adsorption of linear poly(ethylene oxide) on silica surfaces has previously been investigated as a function of pH.[14] The key finding is that poly(ethylene oxide) adsorbs readily at low and neutral pH, but the adsorption decreases sharply in the alkaline pH range. Similar results are obtained for adsorption of alkyl ethoxylates on silica[34] and for ethylene oxide containing block copolymers.[35] These results are very similar to our finding for the adsorption of PEO$_{45}$MEMA:METAC-2, giving strong support to the view that the nonelectrostatic affinity between the PEO-chains of PEO$_{45}$MEMA:METAC-2 and silica is the key factor that determines the adsorption behavior. It is also clear that the nonelectrostatic surface affinity decreases sharply with increasing pH, and it seems very plausible that this is a direct result of the increasing charge density of the silica surface. The magnitude of the surface charge density in 0.1 mM 1:1 electrolyte increases from 3.2 mC/m^2 at pH 6 to 67.3 mC/m^2, or 0.42 nm^2 per charge at pH 10.[24] The latter value corresponds to only 10% of the silanol groups. We conclude that poly(ethylene oxide) interacts favorably with protonated silanol groups, but not with dissociated ones. Further, a rather limited dissociation of the silanol groups is sufficient to completely suppress the adsorption of poly(ethylene oxide) as well as the cationic PEO$_{45}$MEMA:METAC-2. This rationalizes the fact both that adsorption takes place at the isoelectric point of silica and that adsorption is prevented when the surface charge density of silica is high. It is now tempting to conclude that electrostatic interactions are unimportant for the adsorption of PEO$_{45}$MEMA:METAC-2 to silica. However, as will be shown below, this is incorrect and also electrostatic interactions are of importance.

Effect of Ionic Strength on Adsorption of Poly(ethylene oxide) Containing Polymers to Silica. The effect of ionic strength on the adsorption of poly(ethylene oxide) has been investigated previously, and it was found that the adsorbed amount decreased with increasing salt concentration.[36] However, the effect of the ionic strength was found to be considerably less dramatic than in the present case.

We note that at constant pH the silica−water interface develops a higher negative charge density with increasing electrolyte concentration due to a reduced free energy penalty for creating a charged interface with its associated counterions.[37] By using data for the surface charge densities of silica obtained from potentiometric titrations,[24] it can be calculated that at pH 6 the surface charge density increases approximately 3 times from 3.1 to 9 mC/m^2 upon increasing the monovalent electrolyte concentration from 0.1 to 10 mM. Our data show that this results in a decreased affinity between the cationic PEO$_{45}$MEMA:METAC-2 and the increasingly negatively charged surface (see Figure 4). While the adsorbed amount decreases profoundly with increasing $NaNO_3$ concentration at pH 6, only a weak dependence was found at pH 2, particularly at higher ionic strength. Since the silica surface is uncharged at pH 2, adding $NaNO_3$ does not lead to a significant change of the surface charge, which explains the observed weak dependence on electrolyte concentration at this pH. At pH 6, however, the increased salt concentration results in an increased silica surface charge and a decrease in the nonelectrostatic affinity between the PEO chains and the surface. It should also be pointed out that light scattering and small-angle neutron scattering studies revealed that the solution conformation of PEO$_{45}$MEMA:METAC-2 is unaffected by adding salt.[38] Hence, the effects discussed here cannot be attributed to changes in the bulk polymer conformation.

From these data, however, we cannot rule out that a decreased electrostatic affinity between the charged monomers and the surface plays a role for the decreasing surface excess with increasing ionic strength. In particular, we note that Hansupalak and Satore[27] found an extremely sharp decrease in adsorbed amount for an electrostatically driven polyelectrolyte adsorption when the surface was highly charged, and the polyelectrolyte had a low charge density, which is rationalized by competition between polyelectrolyte charges and similarly charged small ions at the surface. However, the decrease in polyelectrolyte adsorption in the study of Hansupalak and Satore was observed at significantly higher ionic strengths than in the present study.

In the present study there are two observations that indicate that electrostatic interactions have importance for the adsorption of PEO$_{45}$MEMA:METAC-2 on silica. First, the maximum adsorption is not realized at pH 2 but rather at pH 4−6 (see Figure 5). Second, inspection of Figure 8 shows that the sensed mass registered by the QCM-D decreases slightly between pH 2 and pH 6, which, together with the higher surface excess at pH 6, suggests a denser layer with lower water content at pH 6 compared to at pH 2. To test whether the electrostatic affinity played a role for the adsorption, an uncharged homopolymer of PEO$_{45}$MEMA was synthesized under conditions identical to those described above for PEO$_{45}$MEMA:METAC-2. The surface excess of this uncharged polymer on silica at pH 6 was found to be about 0.6 mg/m^2, as compared to 1.7 mg/m^2 for PEO$_{45}$MEMA:METAC-2. Increasing the ionic strength to 10 mM, keeping the pH at 6, resulted in a decrease in surface excess to 0.1−0.2 mg/m^2 for PEO$_{45}$MEMA. Thus, we conclude that the small amount of positive charges on PEO$_{45}$MEMA:METAC-2 does have a pronounced effect on the adsorption, but the strong influence of the ionic strength remains for the uncharged polymer. We note that introduction of a small amount of charges also strongly enhances the adsorption of acrylamide-based copolymers to silica[39] and montmorillonite,[40] which is well understood.

The extraordinary sensitivity of the surface excess on electrolyte concentration in the present case is suggested to be due to two effects. First, the nonelectrostatic surface affinity is reduced as the surface charge density is increased. Second, the concentration of small ions at the surface increases with increasing surface charge density, which promotes replacement of polyelectrolyte charges at the surface with small ions having the same sign of charge as the polyelectrolyte. This replacement is enhanced by the fact that the polyelectrolyte charges have difficulties in reaching the silica surfaces due to the presence of 45 units long EO chains on the polyelectrolyte backbone at high graft density.

Origin of the Nonelectrostatic Affinity between the Poly(ethylene oxide) Grafts and Silica. The conventional explanation for the nonelectrostatic affinity between poly(ethylene oxide) and silica is that it is due to hydrogen-bond formation between surface Si−OH groups and the ether oxygen in the polymer chain.[14,41] We note that at the pH where adsorption is suppressed only about 10% of the total amount of silanol groups is charged, and it appears unlikely that such a small reduction in hydrogen-bonding groups can lead to the dramatic reduction in adsorbed amount. However, if it is the isolated silanol groups that are the primary hydrogen-bonding centers to poly(ethylene oxide), as can be rationalized by the fact that they can form hydrogen bonds without breaking already existing intrasurface bonds, it turns out that about 50% of these sites are dissociated at pH 10 (10% of the total silanol content). This could certainly have a serious impact on the hydrogen-bonding ability of the silica surface and thus the adsorption of poly(ethylene oxide) as well as of PEO_{45}MEMA:METAC-2.

Although, the above concept explains the results well, it deserves some further consideration. It is well established that the silica surface is strongly hydrated. Adsorption from aqueous solutions via hydrogen bonding thus involves a displacement of water that forms hydrogen bonds with silica. It can be argued that this is energetically unfavorable. Furthermore, the adsorbing polymer side chains are themselves hydrated, a clathrate-like hydration model has been proposed,[42] and therefore the adsorption proceeds via dehydration of both the surface and the polymer. We note, however, that releasing small water molecules into solution upon polymer adsorption is an entropically favorable process since the loss of conformational entropy associated with the polymer immobilization at the interface cannot offset the entropy gain due to release of a large number of small molecules. Furthermore, the displaced water molecules form hydrogen bonds with each other in solution, which should be taken into account in the free energy balance of adsorption. In fact, Trens and Denoyel[43] have shown that the enthalpy of displacement of water for PEO on silica is −3 kJ/mol of segments, which shows that the adsorption process is enthalpically favorable. We emphasize, however, that it is not sufficient to look at the direct hydrogen bond formation between the Si−OH group and the ether oxygen to grasp the full picture of the free energy change occurring upon adsorption of poly(ethylene oxide) containing polymers and surfactants to silica. Rather, the enthalpy of all broken and formed hydrogen bonds must be considered together with the entropy changes.

Before concluding this section, we note a study by Iler,[31] who measured the hydrogen-bonding effectiveness of poly(ethylene oxide) as a function of the degree of polymerization. Even for short chains the hydrogen-bonding effectiveness increases sharply with the number of ether oxygens. PEO_{45}MEMA:METAC-2 has a high graft density of relatively long PEO chains (45 EO units per side chain). It can be argued that a molecule rich in ether oxygen would possess the high hydrogen-bonding effectiveness necessary for formation of multiple hydrogen bonds with the silica surface.

Effect of the Type of Cation in the Added Salt. As pointed out by Iler,[31] Na^+ ions adsorbed at the surface can displace hydrogen-bonded polyethers. The sodium ion is strongly hydrated in solution, and the large hydration shell may block neighboring silanol groups and decrease the probability of hydrogen bond formation. Indeed, preliminary experiments conducted in the presence of Cs^+ (not shown here), which is significantly less hydrated than Na^+, showed that the adsorbed amount of PEO_{45}MEMA:METAC-2 increases by approximately 20% compared to the adsorbed amount in the presence of equal molar amount of Na^+. The counterion specificity clearly deserves additional attention.

Sticking Probability. The reflectometry measurements were conducted in stagnant point flow, and the kinetic results from different experiments are directly comparable since the adsorbate is transported to the surface by diffusion only (which is not the case for QCM-D where the polymer was introduced simply by exchanging the volume of the liquid cell several times in an uncontrolled flow). From the adsorption data obtained for solution containing 10 ppm PEO_{45}MEMA:METAC-2, it was determined that the initial slopes of the surface excess vs time plots were 0.024 mg m^{-2} s^{-1} at pH 2, compared to 0.0065 mg m^{-2} s^{-1} at pH 6. This much faster initial increase of the adsorbed amount with time at the lower pH value can be attributed to a higher probability that a polymer that reaches the surface will adsorb (the sticking probability) at the lower pH value.

Conclusions

The adsorption of cationic PEO_{45}MEMA:METAC-2 onto silica was studied using reflectometry, QCM-D, and contact angle measurement techniques as a function of pH and ionic strength. It is found that the surface excess, at constant ionic strength, decreases with increasing pH. It is also found that at a constant pH the surface excess decreases with increasing ionic strength of the solution. Hence, contrary to what is found for most polyelectrolytes (note however the results presented in ref 27), the adsorption of the PEO_{45}MEMA:METAC-2 comb polyelectrolyte decreases as the charge density of the oppositely charged silica surface is increased. This finding is rationalized by the combination of a reduction in the nonelectrostatic affinity between PEO chains and silica and competition between small ions and polyelectrolyte charges at the silica surface. It is suggested that the nonelectrostatic affinity between silica and PEO_{45}-MEMA:METAC-2 is facilitated by formation of hydrogen bonds between the ether groups in the side chains of the polymer and protonated silanol groups at the silica−water interface. It is further suggested that hydrogen bonding occurs primarily at isolated silanol groups, which constitute only a fraction of the total number of surface silanol groups. Our results also show that electrostatic interactions between the low number of charges on the polymer backbone and the surface have importance for the adsorption process but that the presence of the side chains enhances the sensitivity to added electrolyte since it counteracts a close approach of the polyelectrolyte charges to the silica surface.

By comparing results from reflectometry and QCM-D techniques, it is evident that the water content of the adsorbed layer is high; about 80% of the sensed mass monitored by the QCM-D technique is due to this water. At pH $>$ 6 the polymer adsorbs in less compact conformations with a large fraction of segments protruding into solution. This results in an increase in the dissipation value and the water content of the layer. At the same time the water contact angle is reduced.

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